A study on the hydration rate of natural zeolite blended cement pastes

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Abstract

Natural zeolite is a type of mineralogical material containing large quantities of reactive SiO_2 and Al_2O_3. It is widely used in the cement industry in China as a cement blending material. Like other pozzolanic materials such as silica fume and fly ash, zeolite contributes to concrete strength mainly through the pozzolanic reaction with $Ca(OH)_2$. Thus, the pozzolanic reactivity of this type of material in comparison with other pozzolans is of much interest. This paper presents experimental results on the compressive strength, degree of pozzolanic reaction, and porosity of zeolite modified cement pastes. These results are compared with those obtained from similar blended cement pastes prepared with silica fume and fly ash replacements. Based on the experimental results, it can be concluded that natural zeolite is a pozzolanic material, with a reactivity between that of silica fume and fly ash. Generally, in blended cement pastes with a lower water-to-cementitious materials ratio, the natural zeolite contributes more to the strength of the pastes. But in the pastes with a higher water to cementitious ratio and a lower cement replacement level it undergoes a higher degree of reaction. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Natural zeolite is a type of aluminosilicate mineral containing large quantities of reactive SiO_2 and Al_2O_3 [1]. It is widely used in the cement industry in China as a cement blending material. In China, more than 200 million tons of cement are produced every year, approximately two-thirds of which are manufactured from vertical kilns. For the cement manufactured from vertical kilns, blending materials, such as fly ash, slag, and zeolite, are added to improve the soundness. As natural zeolite is widely available in China, the total quantity of zeolite used for this purpose is as much as 30 million tons per year.

Zeolite is also used as a mineral admixture to produce high performance concrete in China. According to Feng et al., partial replacement of cement by zeolite can improve the properties of concrete [2,3], by increasing concrete strength and preventing undesirable expansion due to alkali–aggregate reactions. A number of research studies have been carried out on zeolite concrete [1–4], including studies on the mechanical and microstructural properties and strengthening mechanism of zeolite on the blended concrete. Also, it has been reported that zeolite reduced the porosity of the blended cement pastes and improved the interfacial microstructure properties between the blended cement paste and the aggregate in the produced concrete [2].

It is generally considered that zeolite contributes to concrete strength mainly through the pozzolanic reaction with $Ca(OH)_2$, like other pozzolanic materials such as silica fume and fly ash. The pozzolanic reactiv-

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Table 1
Chemical composition of the cement and natural zeolite

Properties	Portland cement	Natural zeolite
SiO_2	19.61	72.03
Al_2O_3	4.82	11.90
Fe_2O_3	3.32	0.67
MgO	2.54	1.19
CaO	63.92	1.69
SO_3	2.63	0.03
Loss on ignition	1.86	7.09
Total	98.70	94.60

ity of this type of material when compared to the other pozzolans is thus of much interest to cement scientists and concrete technologists. Although studies by Li et al. [6] and Poon and co-workers [9,10] determined the reactivity of silica fume and fly ash in the cementitious system, few studies have been carried out on zeolite.

This paper presents experimental results on the compressive strength, degree of pozzolanic reaction, and porosity of zeolite blended cement pastes. The results are compared with the results obtained from smaller studies on silica fume and fly ash blended cement pastes, and are expected to lead to a better understanding of the properties of zeolite concrete.

2. Experimental details

2.1. Materials

The cement used in this study was a commercially available Portland cement equivalent to ASTM Type I. The zeolite used was a mineral admixture commercially available from China. It was composed of the finely divided powder of natural zeolite rock ground with a small percentage of other inorganic materials [2,4]. The principal mineral constituent in the natural zeolite is clinoptilolite. The physical and chemical properties of the cement and zeolite are given in Tables 1 and 2.

2.2. Preparation of samples

The cement/zeolite pastes were prepared at two water-to-cementitious materials ratios (W/CM): 0.25 and 0.3. Zeolite was used as a direct replacement of cement on a weight to weight basis at the levels of 0%,

Table 2
Physical properties of the cement and zeolite

Properties	Portland cement	Natural zeolite
Density	3.15	2.91
Specific surface area (cm^3 g^{-1})	3519	3980

15%, and 25%. The prepared cement/zeolite ceme pastes were cast in 70.7-mm standard cube moulds. T samples were removed from the moulds after 1 day a: were then cured in water at 27°C until the age strength testing.

The samples for the degree of hydration and porosi testing were obtained from the fractured pieces aft the strength test. The fractured pieces were immed ately soaked in acetone for 7 days to stop the hydratio of the cementitious materials. The samples were place in a vacuum desiccator overnight to remove the ace tone and then dried at 60°C in an oven for 24 h. Th dried samples were used for the porosity test. For th determination of the degree of hydration, the driec samples were ground in a mortar to pass through a 150-μm sieve before performing the chemical analysis.

2.3. Compression strength test

The compressive strength of the cubes was tested at the ages of 3, 7, 28, 90, and 180 days using a Denison compression machine at the loading rate of 0.2–0.4 N mm^{-2} s^{-1}.

2.4. Determination of the degree of reaction of zeolite

The determination of the degree of reaction of zeolite was based on a selective dissolution procedure using picric acid–methanol solution and water, originally developed for measuring the degree of reaction of fly ash in the cementitious system [5,6]. The principle of the test procedure in a cement/pozzolana system, is that the pozzolanic material reacts with calcium hydroxide to form acid soluble hydration products. It is possible to dissolve the hydration products of cement and pozzolana and the unreacted cement components, leaving the remaining unreacted pozzolana undissolved [5].

All the calculations described in this section were carried out on the ignited basis (i.e. 1 g of sample was ignited at 950°C in an electric furnace for 1 h). The loss on ignition (LOI) of the zeolite and cement as received, and the dried samples of hydrated pastes was calculated by:

LOI (%) = 100

×(weight of the sample before ignition

−weight of sample after ignition)

/weight of sample after ignition   (1)

The degree of reaction of zeolite was determined by measuring the insoluble residues of the as-received cement and zeolite, and the hydrated zeolite cement pastes when dissolved in a solution of picric acid–methanol–water. One gram of the ground sample

was added to a beaker containing 9 g of picric acid and 60 ml methanol (AR Grade). The mixture was stirred using a magnetic stirrer for 15 min. Of the distilled water 40 ml was added and the mixture was stirred continuously for another 45 min. The mixture was filtered through a Whatman No. 41 filter paper. The filter paper and the residue were washed with methanol until the colour of picric acid disappeared. They were then washed with approximately 300 ml of distilled water at approximately 60°C. The filter paper and its contents were transferred into a porcelain crucible. The crucible was ignited in an electric furnace at 300°C, 450°C and thereafter at 950°C, each for 1 h. The crucible was weighed after cooling to room temperature. The residue per gram of sample on ignited basis was calculated by:

Residue of sample (%)

$$= 100 \times \text{weight of residue/weight of sample} \times (1 - \text{LOI}) \quad (2)$$

The percentage of unreacted zeolite on the ignited basis was given by:

Unreacted zeolite (%)

= residue of hydrated zeolite cement paste

− (residue of as received cement

× original fraction of cement) (3)

The degree of reaction of zeolite was thus given by:

Degree of reaction of zeolite (%)

= 100 × (1 − unreacted zeolite)

/(residue of received zeolite

× original fraction of zeolite) (4)

In Eqs. (3) and (4), original fractions of cement + original fraction of zeolite = 1, also on the ignited basis.

3. Determination of porosity of pastes

The porosity and pore size distribution of the pa samples were measured using a mercury intrus porosimeter (MIP) with a maximum mercury intrusi pressure of 210 MPa. A cylindrical pore geometry a a contact angle θ of 140° were assumed [7,8]. T mercury intruded pore diameter (d) at a pressure (was calculated by, $d = 4\gamma \cos \theta/P$, where $\gamma = 0.4$ Mm^{-1}, the surface tension of mercury.

4. Results and discussion

4.1. Compressive strength

The results of the compression test are shown i Table 3. When compared with the plain Portland ce ment (PC) paste, at the ages of 3 days and 7 day: zeolite replacements slightly reduced the compressiv strength. At the age of 28 days and after, the compres sive strength of the pastes with zeolite replacement wa almost the same as the PC pastes. The zeolite in th pastes with a lower W/CM appeared to contribute better to strength than that in the pastes with a highe W/CM ratio. For example, at the age of 7 days, the pastes with 15% and 25% zeolite replacements with a W/CM = 0.25 achieved strength values equivalent tc that of the PC paste. But those with the same zeolite replacements with a W/CM of 0.3 achieved only 93% of the strength of the corresponding PC paste. This phenomenon is similar to that observed for fly ash blended cement pastes [9,10].

It is noted that the zeolite replacement did not increase the 28-day compressive strength of the blended paste, although a 10% zeolite replacement of cement was reported to increase the 28-day compressive strength of concrete by 10–15% [2]. In fact, the different effects of the pozzolana on the strength of blended cement pastes and concrete were also observed with silica fume replacement [11]. The strength enhancement effect of the silica fume in concrete has been

Table 3
Compressive strength of the zeolite blended cement pastes

Mix		Compressive strength (MPa)				
W/CM	% zeolite	3 days	7 days	28 days	90 days	180 days
0.25	0	73.02	81.91	107.4	120.60	124.73
	15	69.61	81.32	96.01	109.53	127.90
	25	63.50	82.89	103.23	107.33	123.73
0.30	0	62.50	73.26	87.15	105.30	111.87
	15	61.01	68.94	87.75	100.94	117.17
	25	50.31	67.35	90.82	106.50	118.83
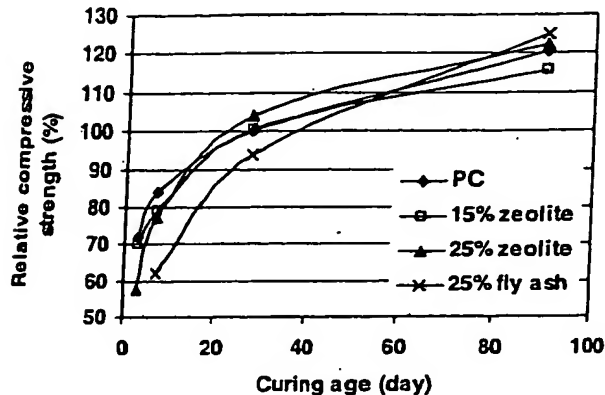
Fig. 1. Compressive strength development of zeolite cement pastes and fly ash cement pastes (W/CM = 0.3).

Fig. 2. Comparison of degree of reaction of natural zeolite with fly ash and silica fume.

attributed to the interfacial bond improvement effect [12].

Fig. 1 shows the compressive strength development of the zeolite/cement pastes and the fly ash/cement pastes, both at a W/CM of 0.3. The strength values are expressed as relative percentages of the compressive strength of the corresponding PC paste at 28 days. The data for the fly ash cement paste are extracted from our other study [10]. When compared with the fly ash blended cement pastes, two observations can be noted: (i) replacement of cement by the natural zeolite resulted in less compressive strength reduction at the early age; and (ii) natural zeolite replacement produced lower strength improvement at the latter ages of curing. These observations indicate the pozzolanic activity of the natural zeolite is significantly different from that of fly ash.

5. Degree of pozzolanic reaction

The degrees of reaction of fly ash and silica fume in the blended cement systems, measured by the same procedure used in this investigation, are reported in another paper of ours [10]. In this paper, the degrees of reaction of zeolite at different ages are presented and are compared with the previous data. At the age of 3 days, a degree of reaction of approximately 5% was recorded for the zeolite (see Table 4). Such a value is similar to that of the fly ash in a fly ash blended cement
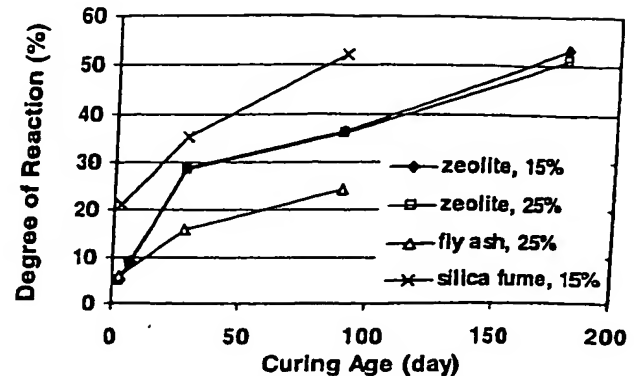
paste with a 25% fly ash replacement. It is, however, lower than that of the silica fume in a silica fume blended cement paste with a 15% silica fume replacement; both with a W/CM of 0.3. At the age of 28 days, the degree of reaction of the zeolite was approximately 29%, while the degrees of reaction of the fly ash and the silica fume were 16% and 35%, respectively [10]. At the latter ages, the degree of reaction of the zeolite was still higher than that of the fly ash but lower than that of the silica fume. At 180 days, approximately 50% of the zeolite had been reacted. A comparison of the degrees of reaction of zeolite with fly ash and silica fume in the different blended cement systems is given in Fig. 2. It can be seen that the reactivity of zeolite is higher than that of fly ash but lower than that of silica fume.

From Table 4, it can also be noted that the degree of reaction of the zeolite in a paste with a higher percentage of replacement is lower than in a paste with a lower percentage of replacement. This is similar to the results in the hydration study of the fly ash cement pastes [9,10].

6. Porosity of the pastes

The results of the MIP test are shown in Table 5. Clearly, the porosity of the pastes decreased as the curing age increased, and increased as the W/CM increased. Compared to the PC pastes, a 15% zeolite

Table 4
Degree of reaction of zeolite in blended cement pastes

Mix		Degree of reaction of zeolite (%)				
W/CM	% zeolite	3 days	7 days	28 days	90 days	180 days
0.25	15	5.20	9.15	29.36	36.15	52.14
	25	4.68	8.44	27.95	35.44	50.16
0.30	15	5.17	9.08	28.94	36.32	53.15
	25	4.93	8.92	28.45	36.14	51.09

Table 5
MIP porosity of the zeolite blended cement pastes

Mix		Mercury porosity (%)				
W/CM	% zeolite	3 days	7 days	28 days	90 days	180 days
0.25	0	12.44	12.32	10.61	9.15	8.72
	15	12.21	12.19	10.10	9.03	8.15
	25	15.22	13.21	12.03	10.04	9.07
0.30	0	12.89	12.64	11.25	9.74	9.25
	15	12.62	12.34	10.45	9.36	8.42
	25	15.69	13.72	12.36	10.28	9.34

replacement resulted in lower porosity at both W/CM ratios and at all ages. This is consistent with the result of Feng et al. [2], who reported that at the age of 28 days the porosity of the paste with 10% zeolite replacement and with a W/CM of 0.3 was lower than the Portland cement paste with the same W/CM. However, it can be noted from Table 5 that when a 25% zeolite replacement was used, the porosity of the pastes was increased at all the studied ages. This indicates that the pore reducing ability of this type of pozzolanic material of cement pastes is limited. Only when a small percentage of replacement is used, the porosity of the paste can be reduced. This is also similar to the effects of fly ash on the porosity of cement pastes, as reported in Poon et al. [13].

It is observed that the difference between the porosity of the paste with 25% zeolite replacement and that of the PC paste was reduced as the curing age increased. For example, at the W/CM = 0.25, the porosity of the paste with 25% fly ash was 22% higher than the PC paste at the age of 3 days, but was only 4% higher than the latter at the age of 180 days. In Fig. 3, relative porosity is defined as the ratio of the porosity of the zeolite blended cement paste to the porosity of the corresponding PC paste.

A decreasing trend of the relative porosity is observed with curing age. Such a trend indicates an increasing degree of pozzolanic reaction in the blended paste took
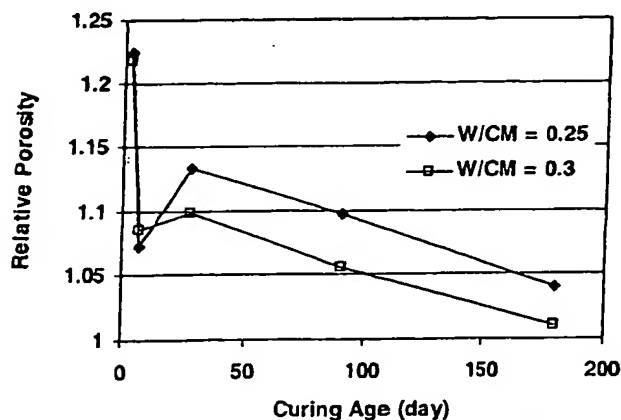
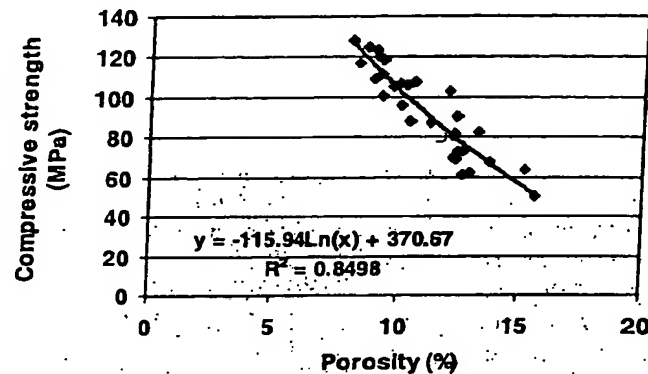

Fig. 4. Correlation of compressive strength and porosity of blende cement pastes.

place with time, with the reaction products filling the pore volume. The porosity data also correlated well with the data on compressive strength (Fig. 4) showing the strength development of the blended cement system is related to the porosity of the cementitious material.

7. Conclusions

In this study, the reactivity of a zeolite mineral admixture, which was prepared from a finely divided powder of natural zeolite rock was investigated. A detailed study on the compressive strength, degree of pozzolanic reaction, and porosity of the cement pastes with and without zeolite replacements has been carried out. Based on the experimental results, it can be concluded that the zeolite used in this study is a pozzolanic material, with the reactivity between that of silica fume and fly ash. In general, zeolite in cement pastes with a lower W/CM ratio contributes more to the strength of the pastes. But in the pastes with a higher W/CM ratio and a lower replacement level it undergoes a higher degree of reaction. A 15% zeolite replacement reduced the porosity of the paste, but a higher replacement level of 25% increased the porosity at all the studied ages from 3 to 180 days. These results are similar to

Fig. 3. Relative porosity of zeolite blended (25%) cement pastes.

that obtained from blended fly ash cement pastes. But as this zeolite is more reactive than fly ash, it resulted in less strength reduction at early ages. However, their strength enhancement property at the longer curing ages is lower than that of fly ash.

As different natural zeolites have different chemical properties and have to be processed to attain a proper fineness before being used in concrete, further investigations are required if the conclusions of this study are to be applied to other natural zeolite sources.

Acknowledgements

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